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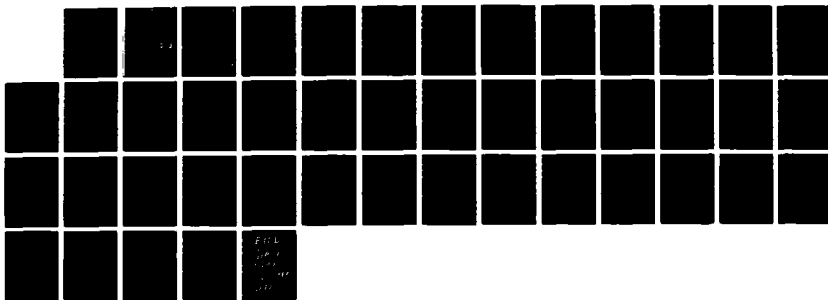
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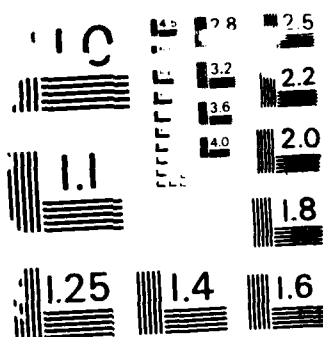
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DEVELOPMENT OF A TEST METHOD TO DETERMINE POTENTIAL PEROXIDE CONTENT IN TURBINE FUELS — PART II

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INTERIM REPORT BFLRF No. 243

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Through the generally accepted 43°C and 65°C bottle storage method of accelerated aging, the relative ratings of six selected fuels' oxidative tendencies were established. In the 43°C test, storage for about 12 weeks produces results that are comparable to a full year's storage under ambient conditions. To develop a practical test method for the prediction of peroxide potential of fuels, experimental conditions were sought so that the oxidative tendencies of fuels could be assessed within a reasonable time. Accordingly, a matrix of experiments was designed to allow selection of reaction conditions that would give results comparable to the bottle storage experiments. Additionally, the results of experiments should allow the development of global reaction kinetics to aid the determination of fuel peroxidation potential and to shed light on the reaction mechanism. The oxidations were carried out in a stirred pressurized reactor at 60°, 80°, 100°, and 120°C, under oxygen pressures of 240, 790, or 1140 kPa (abs) for periods of up to 70 hours.					
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ABSTRACT (Cont'd)

Fuel stressing was done at 60°, 80°, and 100°C under an oxygen pressure of 790 kPa abs, and at 80°C under 1140 kPa abs of oxygen. Additional experiments were carried out at 80°, 100°, and 120°C, under 240 kPa abs of oxygen. Experiments conducted at 60°C for up to 48 hours gave low reaction rates. Results of experiments at 80°C were promising, but the reaction rates were still too low. Oxidation rates at 100° and 120°C were acceptably high, and the results agreed with those of the bottle storage. Interpretation of Arrhenius plots offers a solution to project objectives.

FOREWORD

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I. INTRODUCTION

From 1962 to 1983, both the United States Navy and some commercial air carriers experienced fuel system failures in jet aircraft flying in the Western Pacific. It was shown by Shertzer (1)* and Hazlett, et al. (2) that these difficulties correlated with peroxides in the fuel. Love, et al. (3) also described similar effects of fuel peroxides. It is now known that peroxides attack the neoprene, nitrile, and Buna-N diaphragms and O-rings used in the fuel pumps of jet engines.

To avoid similar problems in the future, a program was initiated to study peroxides and ultimately develop a timely method of predicting the potential peroxide content of jet fuels. It is well known that peroxides form in fuels by an oxidation process that is relatively slow at room temperature. At higher temperatures, the rate of fuel oxidation is dramatically increased. However, it is not certain that the reaction mechanism responsible for peroxide formation is the same at elevated temperatures as it is at ambient temperature. Test methods of determining the oxidative stability of fuels are carried out at elevated temperatures in order to decrease the time required by the test to an acceptable level. It is apparent that an accelerated high-temperature test is also required for the determination of a fuel's tendency to form peroxides.

Since the objective of this study was to provide a basis for a practical test method taking less than 48 hours, the foremost goal was to determine if the mechanism of peroxide formation is the same at elevated temperatures as it is at ambient temperature. Assuming that the kinetics of peroxide formation are similar over a limited temperature range (e.g., 0° to 150°C), it is theoretically possible to predict ambient temperature behavior from high-temperature (e.g., 100°C) measurements.

In the present study, the kinetics of peroxide formation in six kerosenes were examined at elevated temperatures and compared with results obtained at 43° and 65°C.

* Superscript numbers in parentheses refer to the List of References at the end of the report.

II. APPROACH

To achieve the basic goals, experimental conditions were selected to give quick results that correlate with those of the 43° or 65°C bottle storage experiments and serve as a basis for the development of global reaction kinetics to aid in the determination of fuel oxidation potential and to shed light on the reaction mechanism of kerosene oxidation. The matrix of experimental conditions is shown in TABLE 1.

TABLE 1. Test Matrix

Fuel No.	Stess Temperature, °C/Oxygen Pressure, kPa					
	43*	60	65*	80	100	120
0464	21	790	-	790 & 1140	240 & 790	240
11310A	21	790	-	790 & 1140	240 & 790	240
11381	21	790	-	790 & 1140	240 & 790	240
11381A	21	790	-	790 & 1140	240 & 790	240
AV-284	-	-	21	-	240 & 790	240
AV-285	-	-	21	-	240 & 790	240

* Bottle storage tests using ambient air; all other tests under oxygen pressure between 240 and 1140 kPa abs.

As indicators of the extent of oxidation, the oxygen consumption, peroxide content, and formation of gum, water, and acidity were measured. The oxidations under oxygen pressure were carried out in a stirred, pressurized reactor in which the temperature was held constant to within $\pm 0.5^\circ\text{C}$.

Six kerosenes were selected for the study. One of these fuels (No. 0464) was a straight-run, salt-dried, and clay-treated, additive-free Jet A, and was chosen to serve as a pristine, stable fuel (TABLE 2). Four hydrocracked kerosenes were selected as potentially unstable fuels. Two of the reactive fuels were also percolated through a column of activated alumina to remove the native peroxides and some of the other polar components. Since one of the hydrocracked kerosenes (No. 11310) contained over 400 ppm of peroxides, it was alumina treated before use

in experiments. Another hydrocracked fuel (No. 11381) had negligible peroxides so it was used in the experiment both before and after the alumina treatment. Two additional fuels (AV-284 and 285) were also oxidized at 100° and 120°C under 240 kPa (abs) of oxygen.

TABLE 2. Model Fuels

Fuel No.	Description
0464	Jet A, Straight-Run, Additive-Free, Salt-Dried, Clay-Treated
11310A	Hydrocracked Kerosene, Alumina Treated
11381	Hydrocracked Kerosene
11381A	Alumina-Treated Fuel No. 11381
AV-284	Hydrofined Kerosene
AV-285	Hydrocracked Kerosene

Chemical reactivity, including oxidizability of a fuel, depends upon the fuel's chemical composition. Thus, in addition to ASTM-type analyses, a hydrocarbon-type analysis was also performed on each of the model fuels by proton (^1H) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The proton-type assignments were made according to the recommendations of Netzel and Hunter of the Laramie Energy Technology Center ⁽⁴⁾, now Western Research Institute.

It may be argued that the rate-determining step in autoxidation reactions is the initial attack on the C-H bond with the ease of hydrogen abstraction determining the overall rate of oxidation. ⁽⁵⁻⁹⁾ Since the order of free-radical stability and attack on the carbon-hydrogen bond is benzylic and allylic $\text{H} >$ tertiary $\text{H} >$ secondary $\text{H} >$ primary H , it was expected that fuels with different oxidative tendencies would exhibit gross differences in their NMR spectra--and that from the NMR spectra their ease of autoxidation could be calculated. Thus far, this expectation has not been fulfilled, as the abundance of reactive sites, as measured by NMR, does not reflect the relatively large differences in the reactivity of the test fuels with oxygen. Apparently these differences in the strengths of C-H bonds in the test fuels are more subtle than expected and cannot be resolved by NMR spectroscopy. This lack of present correlation is obviously due to the complexity of fuel composition.

III. APPARATUS AND PROCEDURES

To establish baseline data on the long-term stability of four of the selected "model" fuels, the generally accepted method of bottle storage at 43°C (10) was used. In this procedure, 200 mL of each of the test fuels were purged with "synthetic" air (21 percent O₂ and 79 percent N₂) at 300 mL per minute for 5 minutes. Then the fuel samples were stored for an extended time in the dark at 43°C in sealed 500-mL amber borosilicate bottles. Such procedure allowed the determination and monitoring of the oxygen concentration in both the liquid and vapor phases. The sealed system also prevented the loss of fuel components during the stress period. After aging periods of 1, 2, 3, and 4 weeks, followed by 4-week intervals, one bottle of each fuel was retrieved for analysis. In addition to the measurement of peroxides, gum, water, and acid number of the fuel, the oxygen content was determined by gas chromatography in both the liquid and vapor phases. If the oxygen concentration in the vapor phase dropped below 10.0 vol%, the remaining bottles of the same fuel were again aerated.

Two fuels designated as AV-284 and AV-285 were received from the Naval Research Laboratory (NRL). These fuels were part of the fuel matrix used in the third Coordinating Research Council (CRC) cooperative test program on hydroperoxide potential of jet fuels. The 65°C bottle storage tests were carried out according to the protocol described by Hall (11) in his instructions to participants.

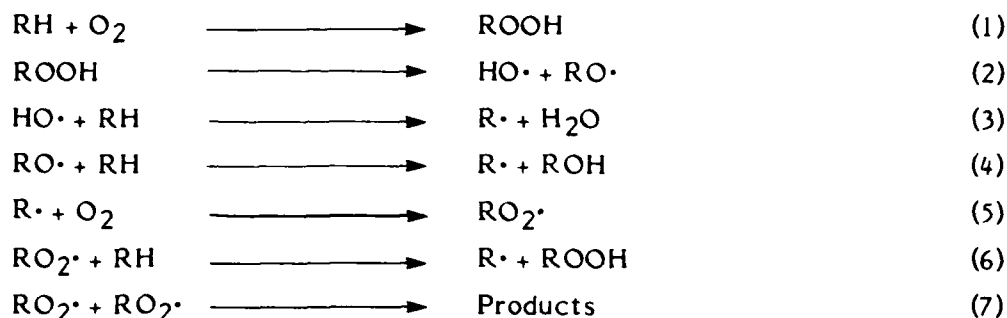
Accelerated oxidative stressing of these fuels was carried out in a pressurized reactor at elevated temperatures. The reactor was made of Type 316 stainless steel and equipped with a magnetically-coupled stirrer driven by a variable speed motor, an external electrical heating element, and an internal cooling loop with automatic temperature control. Valves and fittings permitted introduction of gases and liquids and withdrawal of samples either at the bottom or the top of the vessel. Additionally, the reactor was equipped with a rupture disc, recording temperature probe, and pressure gauge. The reactor was charged with 300 mL of fuel and purged with oxygen of ultra-high purity (99.99 percent min), followed by pressurization to a predetermined pressure, e.g., 740 kPa (abs). While the fuel was stirred at about 150 rpm, the fuel temperature was raised to the test temperature within 20 to 30 minutes, and held there for the test duration within a tolerance of $\pm 0.5^\circ\text{C}$. The pressure and temperature within the reactor were continuously recorded. In early

experiments, a dedicated run was made for each condition. Upon completion of the experiment, the reactor was disassembled at ambient temperature and pressure. All the interior parts were washed, in several increments, with a total of 30 mL of 2-propanol to collect and dissolve all the formed water. These washings were added to the fuel, which was then sparged with argon or nitrogen. The samples were then analyzed for peroxides (ASTM D 3703), gum (ASTM D 381), water (ASTM D 1744), and acid number (ASTM D 664). The adherent and precipitated gums were removed from the reaction vessel by dissolution in an equivolume mixture of toluene, acetone, and methanol. This solvent was evaporated, and the residual gum content was determined by weight.

Subsequently, this test protocol was changed to increase information obtained from each oxidation experiment. Instead of dedicated runs, an aliquot sampling procedure was adopted. Experiments showed that results from the two methods were identical within experimental error. In these later experiments, oxygen pressure in the reactors was maintained at 240 kPa (abs). The time at which the temperature of the fuel reached the set temperature was designated as zero hour. At this time, the first aliquot of sample was withdrawn from the reactor to determine its peroxide number. Sampling was continued at convenient time intervals to measure the buildup of peroxide concentration as a function of time. At the end of this sequence, the residue was analyzed for water, gum, and acidity.

IV. OXIDATION KINETICS

The autoxidation of hydrocarbons is based on a free radical mechanism (12), which includes the familiar radical initiation, propagation, and termination reaction steps. While several reaction steps are conceivable in the overall autoxidation of hydrocarbon fuels, the formation of alkyl peroxides, ROOH, may be described by the mechanism shown in Reactions 1 through 7.



In this mechanism, the alkyl peroxide, ROOH, itself initiates the chain mechanism defined by Reactions 2 through 7.

Free radicals, HO \cdot and RO \cdot , are formed by the decomposition of ROOH in Reaction 2. These radicals react rapidly, forming alkyl radicals, R \cdot , in Reactions 3 and 4. In the presence of oxygen, the alkyl radicals, R \cdot , are rapidly converted to alkylperoxy radicals, RO $_2\cdot$, via Reaction 5. RO $_2\cdot$ is a relatively stable free radical because Reaction 6 is slow compared to Reactions 3 through 5.⁽¹²⁾ Since RO $_2\cdot$ reacts slowly, it tends to build up, and its concentration is much higher than that of the other free radicals. As a result, the radical pool is depleted principally by the recombination of RO $_2\cdot$ in Reaction 7.

In the case of a pristine fuel completely devoid of ROOH, the chain reaction will not start until a trace of ROOH is formed by Reaction 1. While Reaction 1 may be important in starting the autoxidation process, it is relatively slow and contributes very little to the bulk formation of ROOH. Therefore, Reaction 1 may be neglected in the expression below for the rate of formation of ROOH, as shown in Eq. 1:

$$\frac{d(\text{ROOH})}{dt} = k_6(\text{RO}_2\cdot)(\text{RH}) - k_7(\text{ROOH}) \quad \text{Eq. (1)}$$

If the steady-state approximation is made for the free radical concentrations ($\text{HO}\cdot$), ($\text{RO}\cdot$), ($\text{R}\cdot$), and ($\text{RO}_2\cdot$), Eq. 1 may be expressed as

$$\frac{d(\text{ROOH})}{dt} = k_6 \sqrt{\frac{2k_2}{k_7}} (\text{RH}) \sqrt{(\text{ROOH})} - k_2(\text{ROOH}) \quad \text{Eq. (2)}$$

Integration of Eq. 2 over the limits of $(\text{ROOH}) = 0$ to (ROOH) , and $t = 0$ to t gives

$$\ln \left[1 - \frac{k_2}{k_6} \sqrt{\frac{k_7}{2k_2}} \frac{\sqrt{(\text{ROOH})}}{(\text{RH})} \right] = - \frac{k_2}{2} t \quad \text{Eq. (3)}$$

which may be written in approximate form as

$$\sqrt{(\text{ROOH})} = k_6 \sqrt{\frac{k_2}{2k_7}} (\text{RH}) t \quad \text{Eq. (4)}$$

Eq. 4 shows that the formation of peroxides is independent of the oxygen concentration and appears to depend only on the hydrocarbon concentration, which can be assumed to be essentially constant in an autoxidation process. It is important to note ⁽⁵⁾ that, if the concentration of oxygen (partial pressure) is very low (below about 100 mm Hg or 13.3 kPa), Reaction 5 is a rate-controlling step in the mechanism, and Reaction 7 must be replaced by Reaction 8.



In this case, the peroxide concentration may be expressed as

$$\sqrt{(\text{ROOH})} \cong k_5 \sqrt{\frac{k_2}{2k_7}} (\text{O}_2) t \quad \text{Eq. (5)}$$

V. RESULTS AND DISCUSSION

Various methods have been proposed for the evaluation of the storage stability of distillate fuels. These methods include "bottle storage" under an atmosphere of air at 43° and 65°C (10,11) for extended time periods ranging from weeks to months. Since such lengthy procedures are not suitable for quality control, the goal of this project was to find accelerated aging conditions that would quickly yield comparable results.

To establish baseline data, bottle storage tests were performed on all six model fuels. Four of the fuels (Nos. 0464, 11310A, 11381 and 11381A) were treated at 43°C, while the other two fuels (AV-284 and AV-285) were aged at 65°C in bottle storage. The results of these experiments are shown in Figs. 1 and 2. In Fig. 1 the results of bottle storage experiments conducted at 43°C are summarized. The square root of the peroxide concentration in the fuel is proportional to the stress duration. The slope of each line is defined as the global rate constant for the buildup of peroxides. Basically, since the rate is independent of the oxygen concentration, above a threshold oxygen concentration, the global rate constant may be expressed as the combination of rate constants and fuel concentration in Eq. 6

$$k = k_6 \sqrt{\frac{k_2}{2k_7}} (RH) \quad \text{Eq. (6)}$$

where the (RH) is the hydrocarbon, i.e., the fuel concentration. Due to the large excess of this component, it may be assumed to be a constant.

As previously noted, a portion of the work described here was performed in an earlier investigation. The report (13) of that work included results for the oxidative formation of peroxides, water, gum, and acids. This report addresses only the peroxide data obtained, with a more complete listing of results given in the appendix.

The results of the 43°C bottle storage data in Fig. 1 show that the susceptibility of the fuels to peroxide formation increases in the order: Fuel 0464 is essentially unreactive, followed by the possibly inhibited Fuel No. 11381, the alumina-treated Fuel No. 11310, and finally, the alumina-treated Fuel No. 11381.

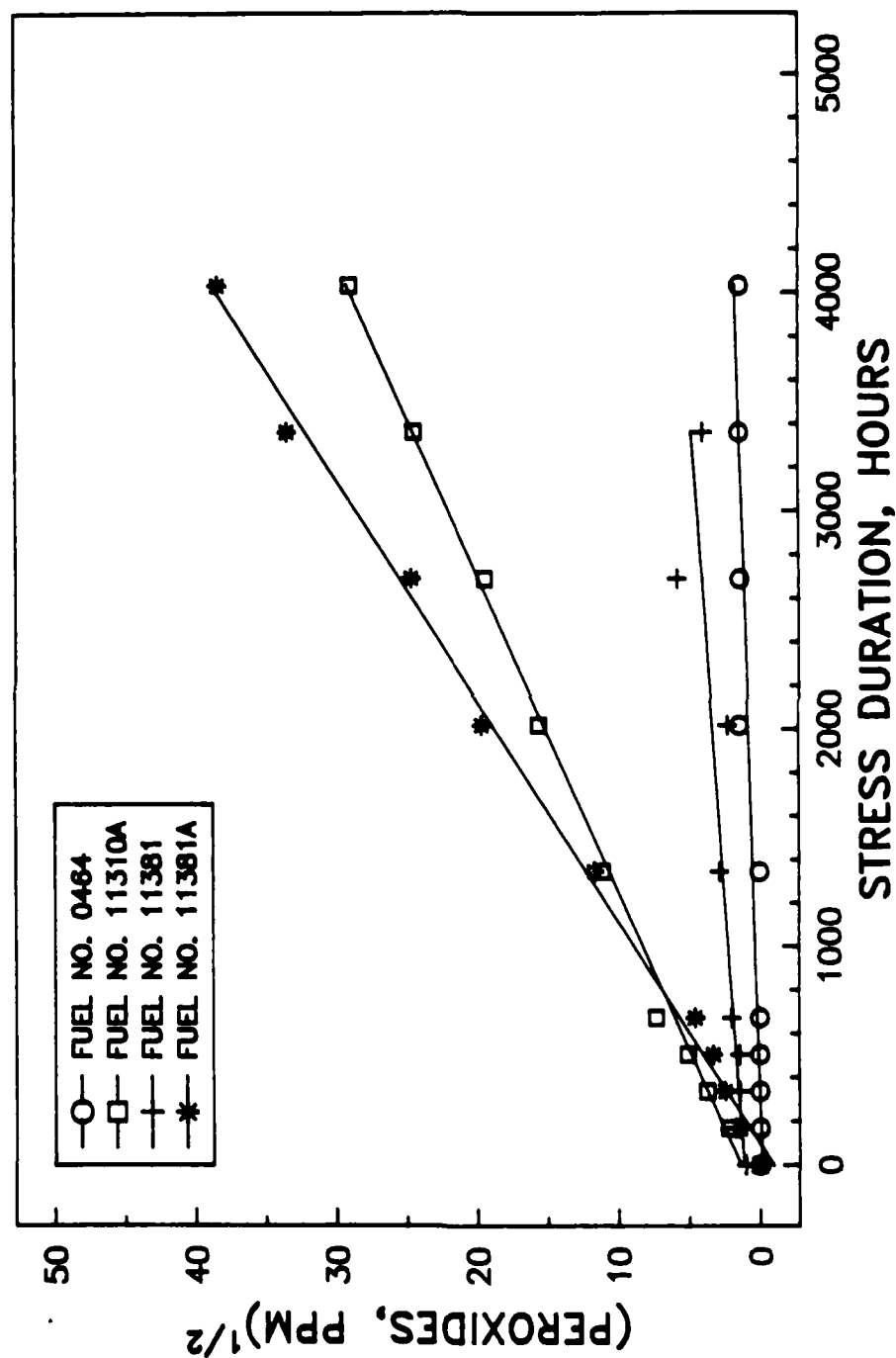


Figure 1. Bottle storage under air at 43°C

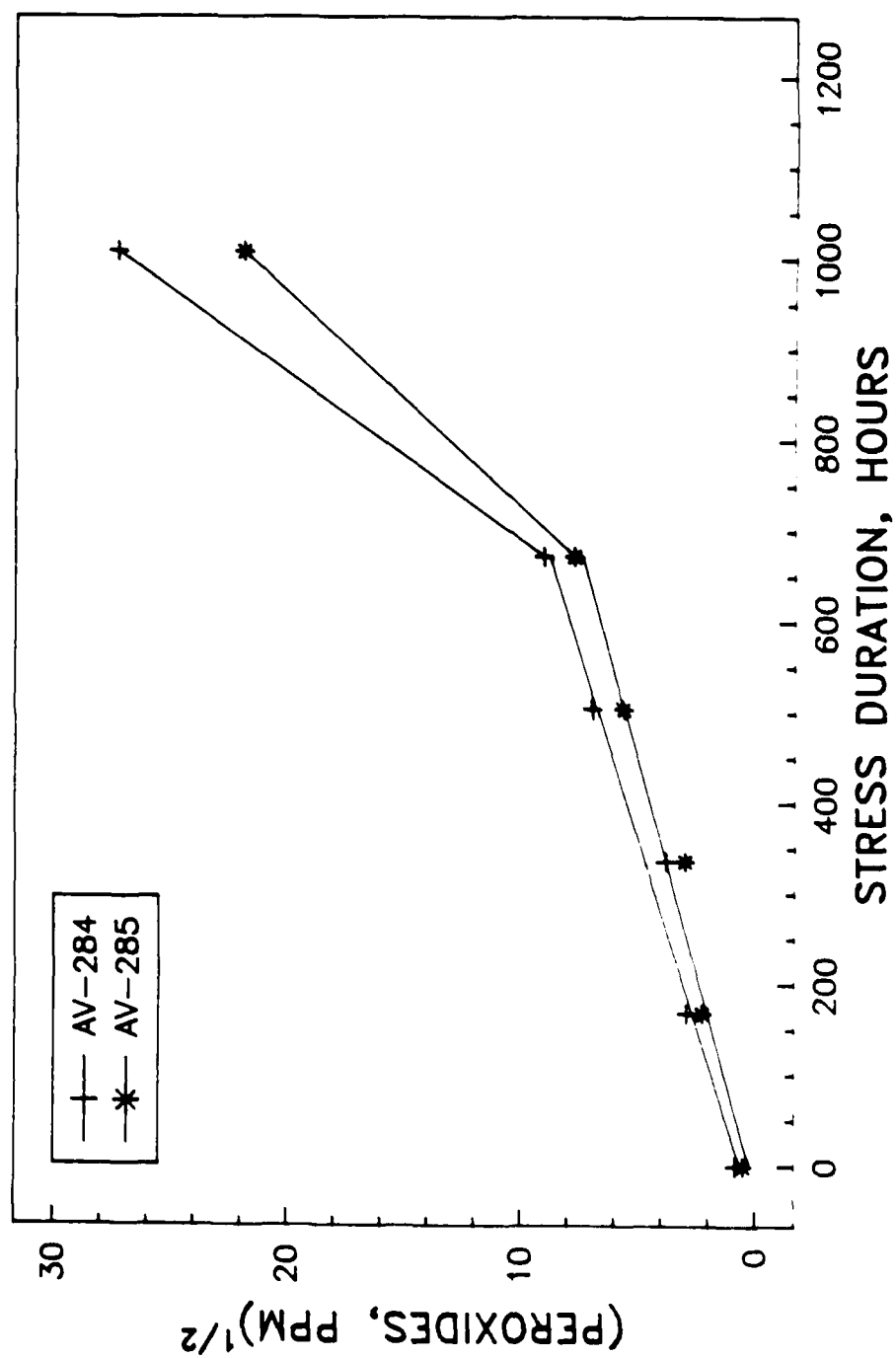


Figure 2. Bottle storage under air at 65°C

Results of bottle storage oxidation experiments at 65°C of fuels AV-284 and AV-285 are graphically presented in Fig. 2. Under these conditions, an induction period lasting for approximately 4 weeks was observed for each fuel. Global rate constants were calculated for both the induction periods and post-induction periods. (The duration of the induction period is arbitrarily taken as the time to reach an inflection point on the concentration versus time curve.)

Similar results were obtained for the peroxide formation in the high-pressure reactor tests at 60°, 80°, and 100°C, i.e., the square root of peroxide concentration was found to be proportional to stress duration. At 60°C, the reaction rates were too low to be of value within the time restraints. At 80°C, the increased reaction rates provided more fuel degradation. However, over 25 hours of stress period was still required for discrimination among the fuels. The results of these experiments are shown in Figs. 3, 4, and 5. The effect of the oxygen pressure on the peroxidation of the four model fuels were addressed at two temperatures. Experiments at 80°C were conducted under 790 and 1140 kPa (abs) of oxygen, while 240 and 790 kPa (abs) of oxygen pressure was used at 100°C. Data indicated that within the experimental constraints of the study, peroxidation of these fuels was independent of oxygen concentration (see TABLE A-2 on p. 31) as under all conditions an excess of oxygen concentration was available. This finding was in agreement with cited literature.⁽⁵⁾ For this reason, Figs. 4 and 5 depict average peroxide values obtained at the respective oxygen pressure pairs. It was found that the rate of the peroxide formation increases quite dramatically with temperature. While peroxides form over a period of several months at 43°C, less than a day is required to form comparable concentrations at 100°C. The relative susceptibilities of the test fuels to form peroxides also change as the stress temperature is increased. This is particularly evident in the changes in the global rate constants of fuels 11381 and 11310A. In the 43°C bottle storage experiment, Fuel No. 11310A is clearly more susceptible to peroxide formation than Fuel No. 11381. The opposite is observed in the 80° and 100°C experiments. This observation proves that rates of peroxidation must be determined at more than one temperature.

Results of oxidations of fuels AV-284 and AV-285 at 100°C are graphically summarized in Fig. 6. Under these conditions, both fuels exhibit induction periods lasting for about 15 hours.

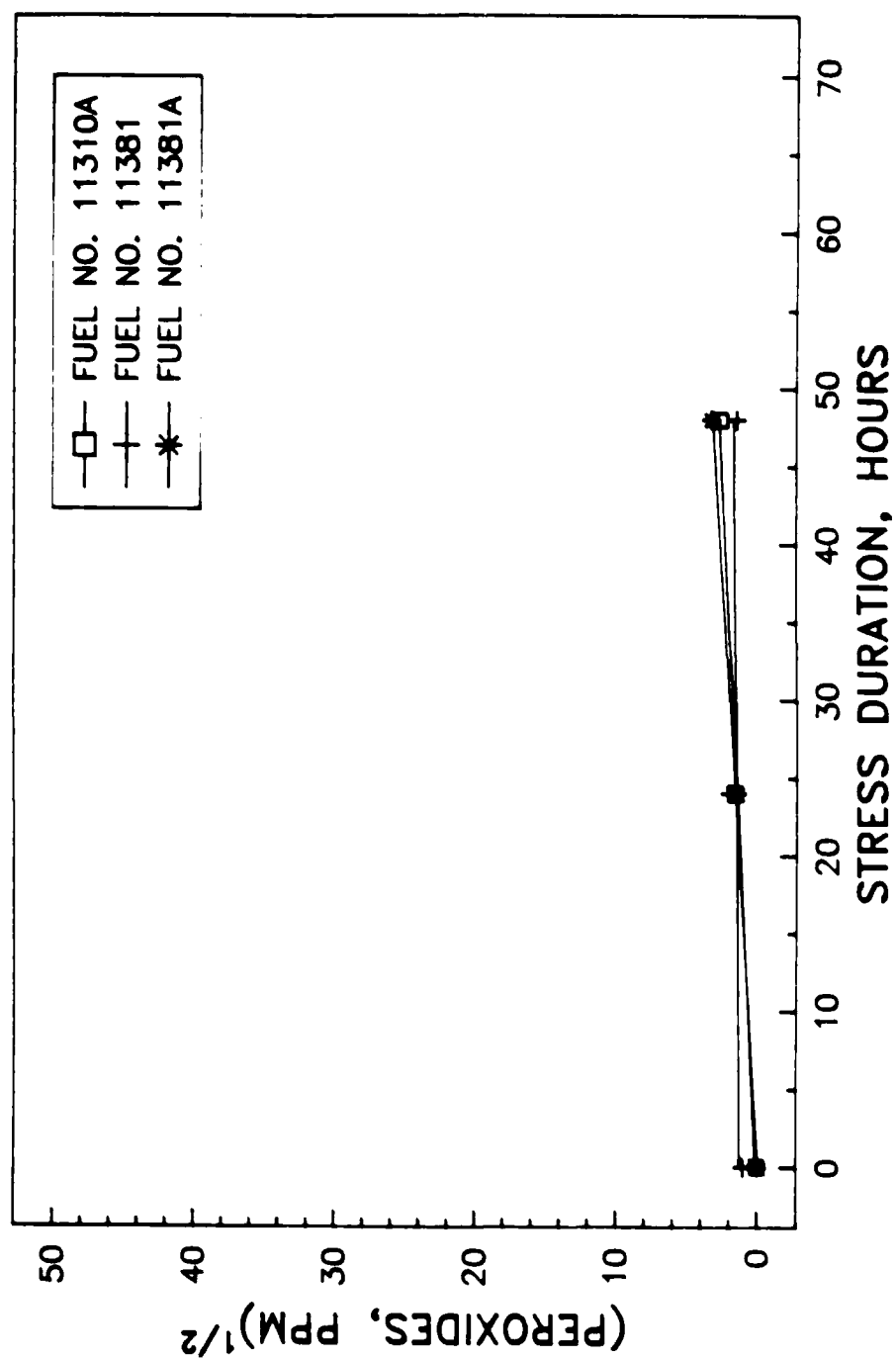


Figure 3. Oxidation at 60°C/790 kPa oxygen

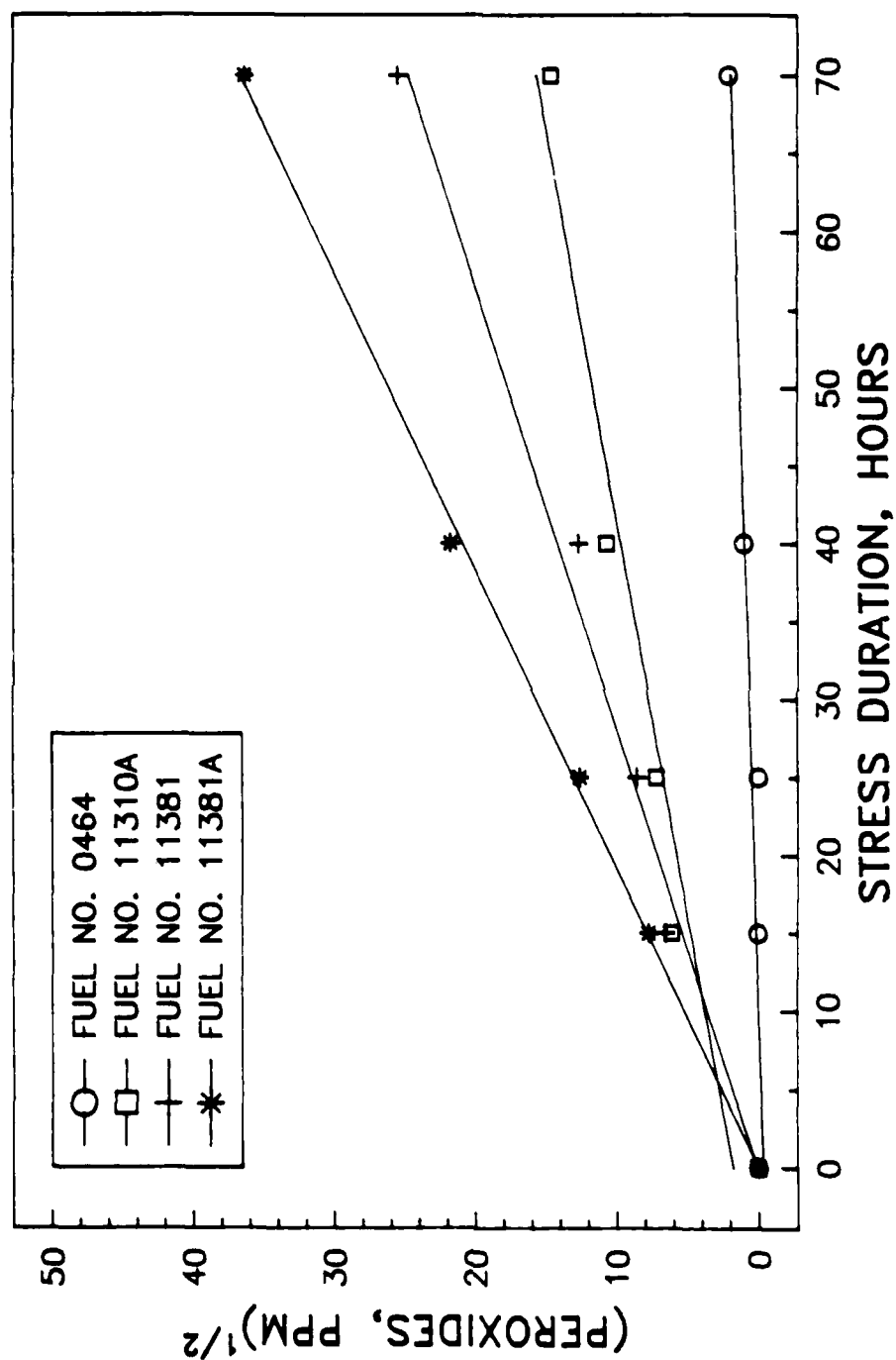


Figure 4. Oxidation at 80°C under oxygen
(Average of 790 and 1140 kPa data)

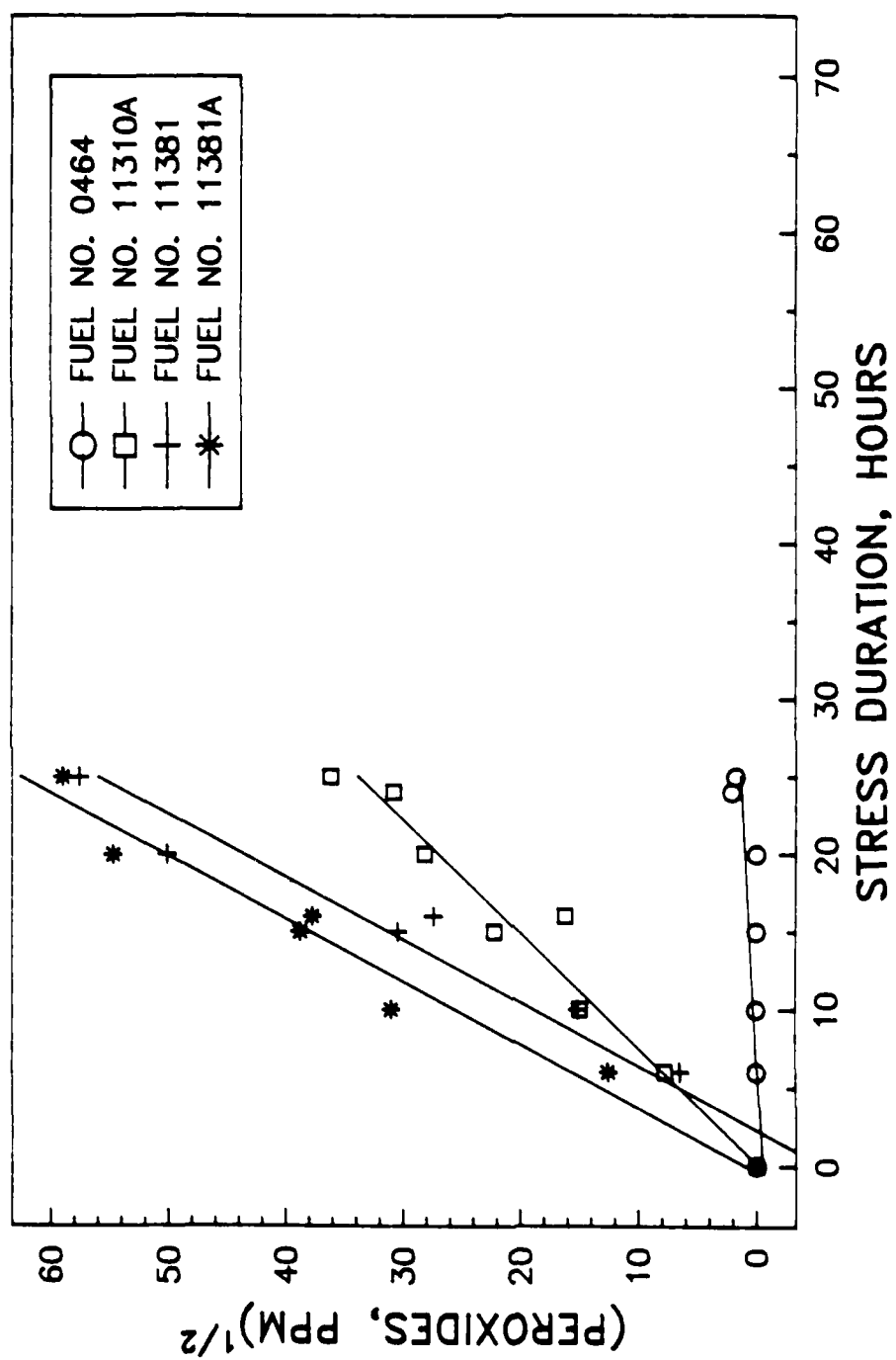


Figure 5. Oxidation of kerosenes at 100°C under 240 and 790 kPa oxygen

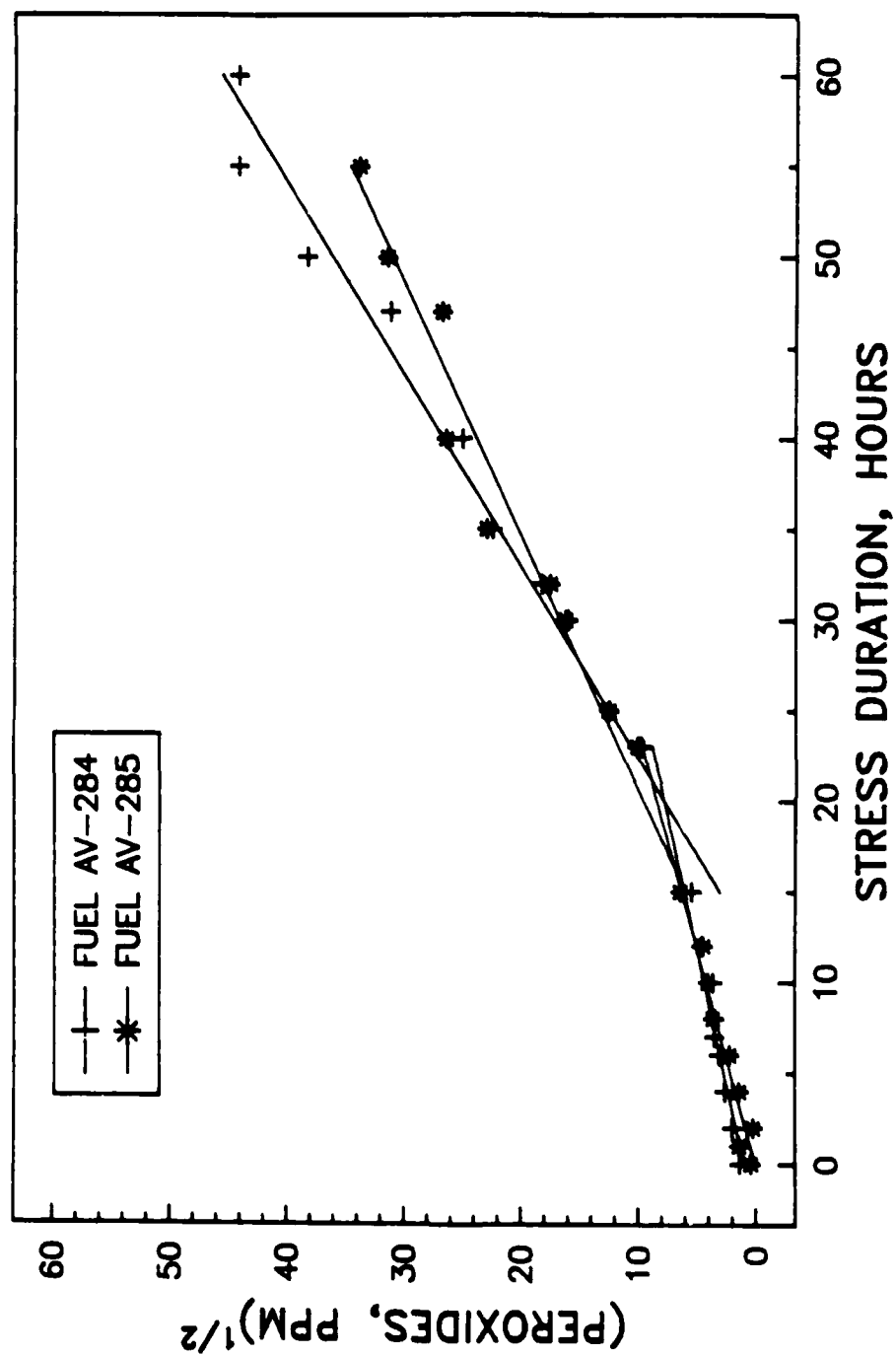


Figure 6. Oxidation at 100°C/240 kPa oxygen

While attempting to determine the global reaction rate constants for the autoxidation of several fuels, it became obvious that for some very stable fuels this task may not be accomplished within a "reasonable" time of about 48 hours at temperatures below 100°C. Relatively stable fuels appear to oxidize at such slow rates that determination of their slope of oxidation (as defined by the increase of the square root of peroxide concentration as a function of stress duration, $\Delta(\text{peroxide conc})^{1/2}/\Delta T$) becomes difficult. Since prediction of potential peroxide concentrations at ambient temperatures depends upon accurate determination of at least two rates at elevated temperatures, the application of temperatures above 100°C had to be explored. Exploratory research was, therefore, conducted at 120°C to determine the rates of oxidation of the six previously used model fuels.

Results of the 120°C oxidation experiments are shown in Figs. 7 and 8. Fuel No. 0464 proved to be a very stable fuel, in which the peroxide concentration is only about 12 ppm after 15 hours of stress. Buildup of peroxide concentrations in Fuel Nos. 11310A, 11381, and 11381A reached over 1000 ppm within 5 to 6 hours. The oxidations of Fuel Nos. AV-284 and AV-285 at 120° show negligible induction periods which is contrary to that at lower temperatures where both fuels exhibited pronounced induction periods. For this reason, data for these fuels are presented separately from that of the other four fuels. In constructing the Arrhenius plots for these fuels, only one global rate constant was available at 120°C; however, at lower temperatures the natural logarithms of two global reaction rate constants were used: one defined by the data generated within the induction period, another for the post-induction period.

The measured global oxidation reaction rate constants for each model fuel at the applicable temperatures are summarized in TABLES 3 and 4. (Data derived from the oxidation of Fuel Nos. 0464, 11310A, 11381, and 11381A are summarized in TABLE 3, while those for Fuel Nos. AV-284 and AV-285 are given in TABLE 4.) The temperature dependencies of the global rate constants for the model fuels between the experimental temperature limits of 43° and 120°C are given in TABLE 5, and in Figs. 9 and 10. Linear regression analysis of the Arrhenius plots is summarized in TABLE 6.

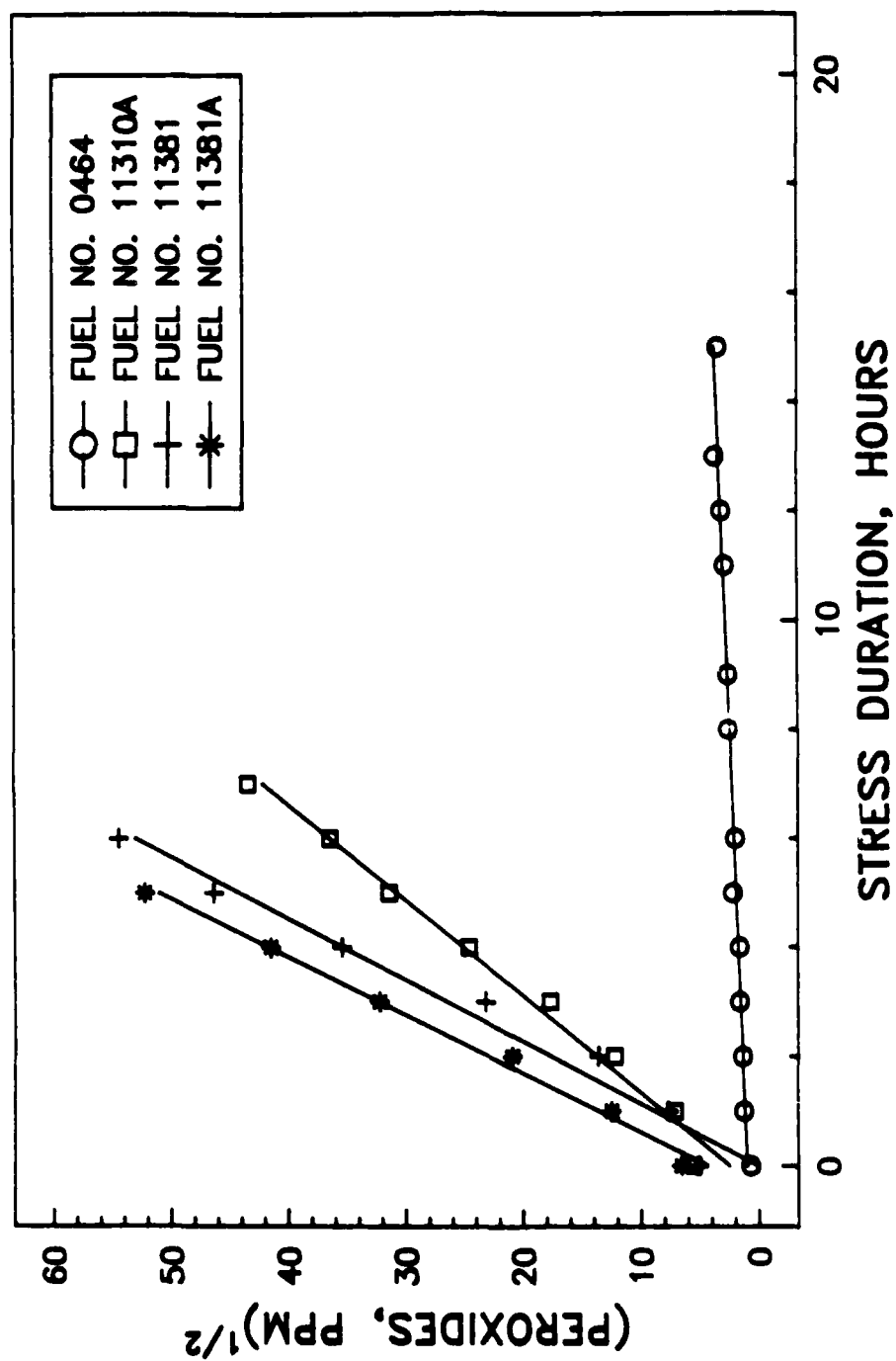


Figure 7. Oxidation at 120°C/240 kPa oxygen — four base fuels

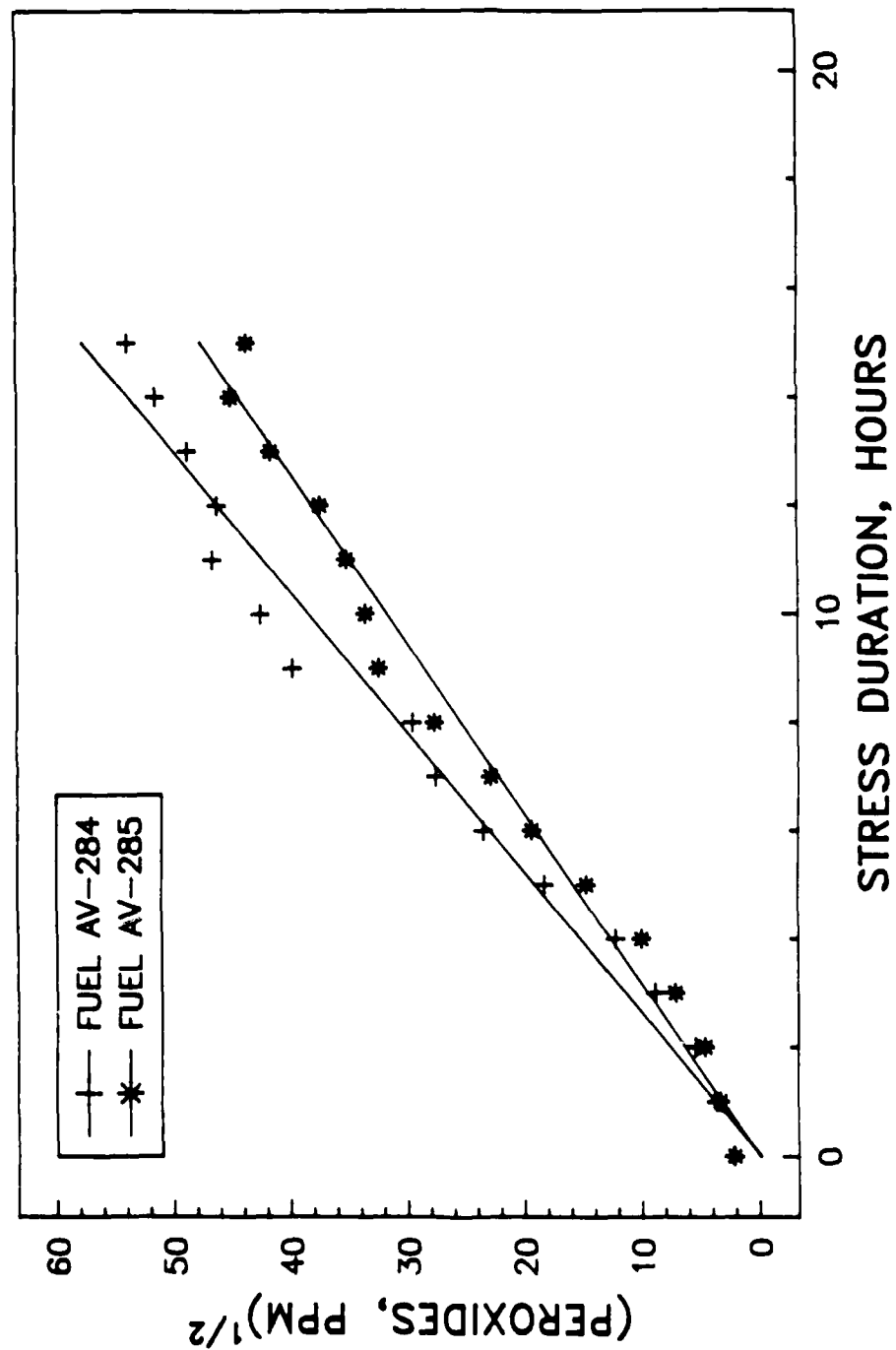


Figure 8. Oxidation at 120°C/240 kPa oxygen — two AV fuels

TABLE 3. Linear Regression Analysis of the Oxidation of Four Kerosenes

Fuel No.	Atmosphere	Pressure, kPa (abs)	Temperature, °C	k	R ²
0464	Air	101	43	4.578×10^{-4}	0.8182
11310A	Air	101	43	6.897×10^{-3}	0.9951
11381	Air	101	43	1.088×10^{-3}	0.7217
11381A	Air	101	43	9.849×10^{-3}	0.9964
0464	Oxygen	790	60	-	-
11310A	Oxygen	790	60	5.396×10^{-2}	0.9841
11381	Oxygen	790	60	8.542×10^{-3}	0.1851
11381A	Oxygen	790	60	6.688×10^{-2}	0.9951
0464	Oxygen	790 & 1140	80	3.068×10^{-2}	0.5946
11310A	Oxygen	790 & 1140	80	2.101×10^{-1}	0.9263
11381	Oxygen	790 & 1140	80	3.508×10^{-1}	0.9781
11381A	Oxygen	790 & 1140	80	5.268×10^{-1}	0.9964
0464	Oxygen	240 & 790	100	7.694×10^{-2}	0.5102
11310A	Oxygen	240 & 790	100	1.386	0.9411
11381	Oxygen	240 & 790	100	2.602	0.9451
11381A	Oxygen	240 & 790	100	2.473	0.9381
0464	Oxygen	240	120	1.814×10^{-1}	0.9586
11310A	Oxygen	240	120	5.663	0.9867
11381	Oxygen	240	120	8.819	0.9727
11381A	Oxygen	240	120	9.329	0.9922

TABLE 4. Linear Regression Analysis of the Oxidation of Fuels AV-284 and AV-285

Fuel No.	Reactor	Atmosphere	Pressure, kPa (abs)	Temp., °C	Time, hr	k	R ²
AV-284	Bottle	Air	101	65	0 - 672	1.222 x 10 ⁻²	0.9656
AV-284	Bottle	Air	101	65	672 - 1008	5.430 x 10 ⁻²	0.9810
AV-285	Bottle	Air	101	65	0 - 672	1.085 x 10 ⁻²	0.9097
AV-285	Bottle	Air	101	65	672 - 1008	4.215 x 10 ⁻²	0.9715
AV-284	A	Oxygen	240	100	0 - 23	3.142 x 10 ⁻¹	0.8182
AV-284	B	Oxygen	240	100	0 - 23	3.721 x 10 ⁻¹	0.7669
AV-284	A&B	Oxygen	240	100	0 - 23	3.423 x 10 ⁻¹	0.7816
AV-284	Avg	Oxygen	240	100	0 - 23	3.409 x 10 ⁻¹	0.9513
AV-284	A	Oxygen	240	100	15 - 60	9.310 x 10 ⁻¹	0.9096
AV-284	B	Oxygen	240	100	15 - 60	1.0055	0.8893
AV-284	A&B	Oxygen	240	100	15 - 60	9.645 x 10 ⁻¹	0.8958
AV-284	Avg	Oxygen	240	100	15 - 60	9.452 x 10 ⁻¹	0.9817
AV-285	A	Oxygen	240	100	0 - 23	4.339 x 10 ⁻¹	0.9497
AV-285	B	Oxygen	240	100	0 - 23	4.309 x 10 ⁻¹	0.9449
AV-285	A&B	Oxygen	240	100	0 - 23	4.268 x 10 ⁻¹	0.9454
AV-285	Avg	Oxygen	240	100	0 - 23	4.216 x 10 ⁻¹	0.9731
AV-285	A	Oxygen	240	100	15 - 55	8.229 x 10 ⁻¹	0.9113
AV-285	B	Oxygen	240	100	15 - 55	7.113 x 10 ⁻¹	0.9431
AV-285	A&B	Oxygen	240	100	15 - 55	7.403 x 10 ⁻¹	0.9363
AV-285	Avg	Oxygen	240	100	15 - 55	7.155 x 10 ⁻¹	0.9707
AV-284	A	Oxygen	240	120	0 - 15	3.8313	0.9577
AV-284	B	Oxygen	240	120	0 - 15	3.8535	0.9784
AV-284	A&B	Oxygen	240	120	0 - 15	3.8386	0.9675
AV-284	Avg	Oxygen	240	120	0 - 15	3.8517	0.9781
AV-285	A	Oxygen	240	120	0 - 15	3.2102	0.9445
AV-285	B	Oxygen	240	120	0 - 15	3.1590	0.9740
AV-285	A&B	Oxygen	240	120	0 - 15	3.1832	0.9548
AV-285	Avg	Oxygen	240	120	0 - 15	3.1708	0.9822

TABLE 5. Temperature Dependence of Kerosene Oxidation

Fuel No.	ln k					
	43°C(a)	60°C	65°C(a)	80°C	100°C	120°C
0464	-7.6891	-	-	-3.4841	-2.5648	-1.7069
11310A	-4.9766	-2.9195	-	-1.5603	0.3265	1.7340
11381	-6.8233	-4.7628	-	-1.0476	0.9564	2.1769
11381A	-4.6203	-2.7049	-	-0.6410	0.9056	2.2331
AV-284	-	-	-4.4044(b)	-	-1.0761(b)	1.3485
AV-284	-	-	-2.9133(c)	-	-0.0564(c)	-
AV-285	-	-	-4.5241(b)	-	-0.8637(b)	1.1540
AV-285	-	-	-3.1666(c)	-	-0.3348(c)	-

(a) Bottle storage

(b) Induction period

(c) Post-induction period

TABLE 6. Linear Regression Analysis of the Arrhenius Plots Based on

$$\ln k = \ln A - (E_a/RT)$$

<u>Fuel No.</u>	<u>Period</u>	<u>Temp. Range, °C</u>	<u>E_a, kcal/mole/K</u>	<u>ln A Factor</u>	<u>R²</u>
0464	Full Range	43 - 120	19.42	23.56	0.9676
11310A	Full Range	43 - 120	21.16	28.82	0.9959
11381	Full Range	43 - 120	30.28	41.46	0.9820
11381A	Full Range	43 - 120	22.04	30.60	0.9977
AV-284	Induction Period	65 - 120	27.04	35.76	0.9893
AV-284	Post Induction Period	65 - 120	20.45	27.54	1.0000
AV-285	Induction Period	65 - 120	27.08	35.78	0.9992
AV-285	Post Induction Period	65 - 120	20.66	27.59	0.9997

Examination of the Arrhenius plots (Figs. 9 and 10) reveals that the global activation energies of the peroxide-forming reactions are of similar magnitude for all but one of the model fuels. The apparent anomalous result given in Fig. 9 shows that the global activation energy for the peroxide formation in Fuel No. 11381 is significantly higher than that of the other fuels. This is the reason why Fuel No. 11381 is very reactive at high temperatures, and relatively unreactive at 43°C. The cause of the higher activation energy is unknown at this time, but it may be due to the presence of a possible antioxidant, or some form of radical scavenger.

The finite differences in the activation energies among the other fuels are important to consider if the susceptibility to form peroxides is to be predicted at ambient conditions from timely experiments at elevated temperatures. It is of importance that the global rate constants for each fuel determined at elevated temperatures under relatively high oxygen pressures strongly correlate with data obtained at 43° and 65°C at relatively low partial pressures of oxygen. These results give no evidence for a change in the mechanisms at temperatures up to 120°C. Also, changing oxygen pressure between 240 and 1140 kPa (abs) was found to have negligible effect on the rate of oxidation. These results support the oxygen concentration independent mechanism described earlier.

In view of the strong correlation between the global rate constants shown in the Arrhenius plots of Figs. 9 and 10, it seems reasonably certain that - at least for the model fuels of this study - the reaction mechanism for the overall formation of peroxides does not change over the temperature range of 43° to 120°C. This is important because it clearly indicates that the susceptibility of a fuel to form peroxides at ambient conditions can be predicted from timely measurements of the rate of peroxide formation at elevated temperatures.

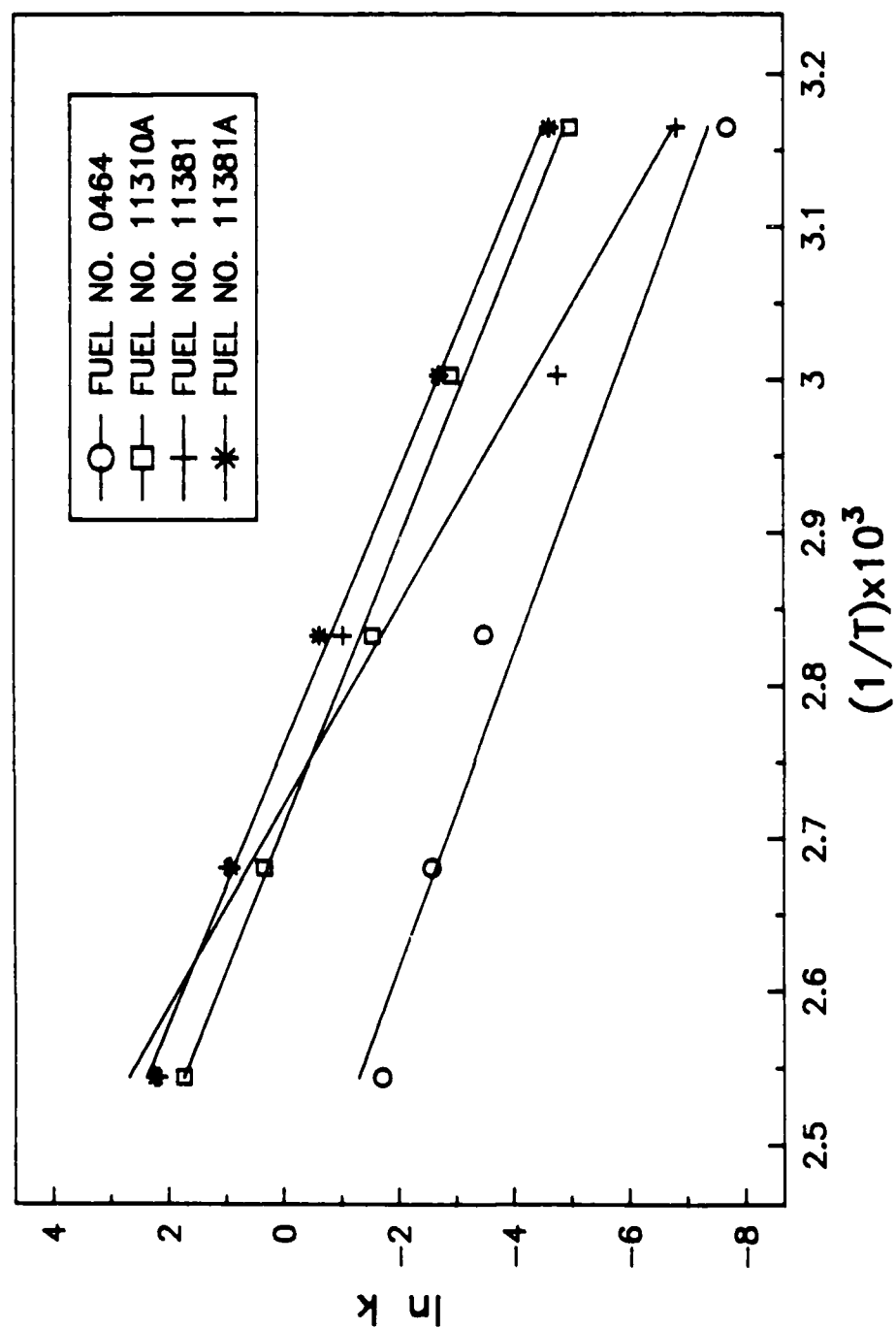


Figure 9. Arrhenius plot of kerosene oxidation — four base fuels

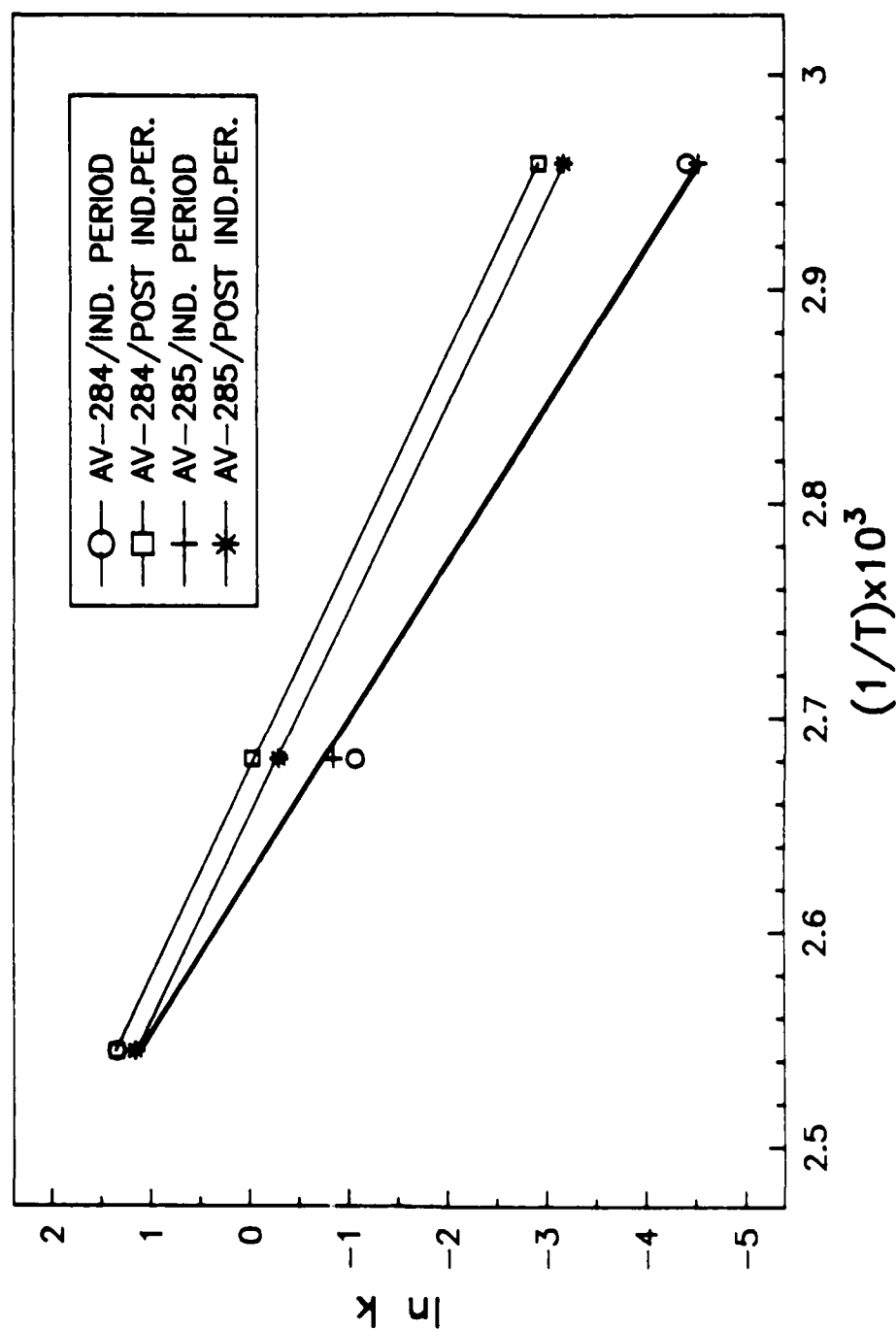


Figure 10. Arrhenius plot of kerosene oxidation — two AV fuels

VI. POTENTIAL PEROXIDE TEST

From the results of this work, it appears possible to determine a characteristic time for the formation of a specified critical peroxide concentration from timely tests carried out on the fuel at elevated temperatures. According to current proposals, a fuel is unacceptable when its peroxide content exceeds 8 ppm. The characteristic time (t) required for 8 ppm of peroxide to form in a fuel at ambient temperature, T_a , may be expressed as

$$t = \sqrt{\frac{8}{k_1}} \left(\frac{k_1}{k_2} \right)^b \quad \text{Eq. (7)}$$

where k_1 and k_2 are the global rate constants determined at elevated temperatures T_1 and T_2 and the exponent, b , is

$$b = \frac{T_2}{T_a} \left(\frac{T_1 - T_a}{T_1 - T_2} \right) \quad \text{Eq. (8)}$$

The global rate constants k_1 and k_2 are determined at high temperatures (e.g., $T_1 = 120^\circ\text{C}$ and $T_2 = 100^\circ\text{C}$) by plotting the square root of the peroxide concentration versus stress duration for each temperature, and taking the slopes of the lines.

VII. CONCLUSIONS

Peroxide formations in six model test fuels were examined in the temperature range of 43° to 120°C with oxygen partial pressures ranging from approximately 20 kPa to 1140 kPa (abs).

From measurement of peroxide buildup, it was found that:

- The square root of the peroxide concentration was proportional to the stress duration.
- The proportionality constant in this relationship was defined as a global rate constant.
- This result was in accordance with a kinetic model, which was based on the assumption that the peroxide itself was the principal free radical initiator.
- The rate of formation of peroxides was found to be strongly temperature dependent, but independent of the partial pressure of oxygen.
- Activation energies ranged from 19 to 30 kcal/mole.
- A strong correlation of the global rate constants with temperature in the Arrhenius plot gives no evidence for a change in the reaction mechanism over the temperature range from 43° to 120°C for the six fuels studied.

The results of this work show that it is possible to predict peroxide buildup in jet fuels at ambient conditions from timely stress tests performed at elevated temperatures.

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APPENDIX
PEROXIDE DATA

TABLE A-1 Bottle Storage Results — All Fuels

Time, hr	(Peroxides, ppm) ^{1/2}					
	<u>0464</u>	<u>11310A</u>	<u>11381</u>	<u>11381A</u>	<u>AV-284</u>	<u>AV-285</u>
	<u>43°C, Air</u>				<u>65°C, Air</u>	
0	0	0	1	1	1.26	1.06
	-	-	-	-	0.28	0.40
	-	-	-	-	0.94	0
168	0	2.24	1.73	1.41	2.95	2.48
	-	-	-	-	3.07	1.88
	-	-	-	-	2.74	1.83
	-	-	-	-	-	2.32
	-	-	-	-	-	2.45
	-	-	-	-	-	2.45
336	0	3.74	1.41	2.45	3.61	2.99
	-	-	-	-	3.86	2.95
	-	-	-	-	4.02	3.1
504	0	5.1	1.41	3.32	6.66	6.1
	-	-	-	-	7.28	5.46
	-	-	-	-	7.03	5.4
672	0	7.35	2	4.58	8.41	7.28
	-	-	-	-	9.25	7.22
	-	-	-	-	9.52	8.9
	-	-	-	-	-	10.02
	-	-	-	-	-	6.02
	-	-	-	-	-	7.09
1008	-	-	-	-	26.64	22.5
	-	-	-	-	25.59	22.27
	-	-	-	-	29.68	20.98
1344	0	11.14	2.83	11.7	-	-
2016	1.41	15.59	2.24	19.65	-	-
2688	1.41	19.49	5.83	24.7	-	-
3360	1.41	24.47	4	33.45	-	-
4032	1.41	29	-	38.35	-	-

TABLE A-2. Accelerated Oxidation Results — Four Base Fuels

Time, hr	(Peroxides, ppm) ^{1/2}			
	0464	11310A	11381	1'381A
60°C, 790 kPa (abs) O ₂				
0	-	0	1	0
24	-	1.58	1.95	1.41
48	-	2.59	1.41	3.21
80°C, 790/1140 kPa (abs) O ₂				
0	0	0	0	0
15	0, 0	6.71, 5.48	6.24, 6.78	7.07, 8.37
25	0, 0	7.62, 6.78	7.07, 10.05	11.83, 13.34
40	1.9, 0	10.63, 10.77	12.69	21.82, 21.68
70	2.09	14.66	25.51	36.33
100°C, 240/790 kPa (abs) O ₂				
0	0	0	0	0
6	0	7.75	6.48	12.57
10	0, 0, 0	14.14, 15.81	11, 17.66,	15.84, 30.84,
	-	-	16.88	31.13
15	0, 0	24.84, 19.65	30.66, 30.82	36.81, 40.62
16	-	16.22	27.39	37.68
20	0, 0	27.29, 29.05	53.17, 47.03	53.69, 55.67
24	2.12	30.81	-	-
25	1.57, 2	38.64, 33.63	57.06, 58.04	57.2, 60.71
120°C, 240 kPa (abs) O ₂				
0	0.71	5.54	5.11	6.55
1	1.26	7.12	7.70	12.51
2	1.38	12.24	13.61	20.96
3	1.61	17.72	23.23	32.21
4	1.61	24.63	35.38	41.46
5	2.19	31.39	46.33	52.23
6	2.00	36.40	54.41	-
7	-	43.39	-	-
8	2.57	-	-	-
9	2.62	-	-	-
11	2.86	-	-	-
12	3.13	-	-	-
13	3.67	-	-	-
15	3.44	-	-	-

TABLE A-3. Accelerated Oxidation Results — Two AV Fuels

Time, hr	(Peroxides, ppm) ^{1/2}			
	AV-284		AV-285	
	React. A	React. B	React. A	React. B
100°C, 240 kPa (abs) O ₂				
0	1.05, 2.02	2.05, 1.8	0,0	1.05, 0.55
1	-	-	1.18	1.64
2	1.9, 2.19	1.73, 1.76, 2.47	0	0, 0.63
4	2.63, 2.49	2.7, 2.86, 2.51	1.64, 0	0.55, 2.05
6	3.27, 2.92	3.67, 2.63	2.14, 2.14	1.72, 2.88
7	-	3.53	-	-
8	3.33, 3.58	3.56	3.11, 3.65	3.10, 4.65
10	4.21, 3.52	3.21	3.48, 3.66	4.32, 4.96
12	5.85, 4.37	3.77	3.70, 4.14	4.72, 5.42
15	6.83, 4.63	5.02	5.33, 7.15	6.21, 7.18
23	6.39, 11.31	14.02, 7.41	9.77, 10.30	10.82, 9.51
25	8.04, 14.66	18.01, 9.26	10.89, 12.37	14.93, 12.00
30	12.21, 19.65	23.71, 12.24, 12.33	15.34, 16.68	17.79, 15.10
32	21.65, 14.39	18.68	15.50, 18.84	16.06, 19.80
35	27.44, 16.03	24.04	19.60, 24.70	21.56, 26.06
40	29.89, 20.23	-	27.20	24.86, 27.33
47	28.39, 32.48	37.12, 26.89	-	26.80
50	36.97, 36.17	45.16, 34.97	-	31.48
55	44.81	46.81	-	35.33, 32.43
60	44.18	-	-	-
120°C, 240 kPa (abs) O ₂				
0	1.97, 1.90	3.58, 1.45	3.93, 2.70	2.02, 0
1	3.18, 3.36	4.14, 3.83	4.20, 4.02	2.35, 2.59
2	5.12, 4.49	5.02, 7.00	4.60, 5.93	3.63, 4.28
3	7.62, 8.14	8.09, 11.47	7.62, 7.25	6.62, 7.00
4	11.67, 10.96	10.95, 15.36	11.51, 11.54	8.96, 8.17
5	15.94	17.04, 21.73	16.41, 14.33	14.96, 13.03
6	20.36	22.22, 27.78	19.00, 20.60	19.13, 18.61
7	-	27.52	24.95	22.51, 20.98
8	31.23, 31.69	28.34, 26.63	27.52, 31.15	25.77, 25.96
9	38.32, 41.93	38.99	27.03, 38.80	32.81, 30.99
10	41.10, 44.41	40.51, 40.81	31.13, 38.45	32.70, 31.77
11	45.86, 43.36	47.38	30.32, 42.20	32.59, 35.32
12	44.95, 48.57	47.19, 43.75	33.75, 39.06	41.05, 35.42
13	47.22, 49.65	49.21	44.00	39.13
14	50.69, 51.81	54.87, 48.51	45.02	-
15	47.21, 51.62	59.54, 56.83	45.04	42.10, 43.70

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